Millimeter-wave-detected, millimeter-wave optical polarization spectroscopy

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We report a new form of microwave optical double-resonance spectroscopy called millimeter-wave-detected, millimeter-wave optical polarization spectroscopy (mmOPS). In contrast to other forms of polarization spectroscopy, in which the polarization rotation of optical beams is detected, the mmOPS technique is based on the polarization rotation of millimeter waves induced by the anisotropy from optical pumping out of the lower or upper levels of the millimeter wave transition. By monitoring ground-state rotational transitions with the millimeter waves, the mmOPS technique is capable of identifying weak or otherwise difficult-to-observe optical transitions in complex chemical environments, where multiple molecular species or vibrational states can lead to spectral congestion. Once a transition is identified, mmOPS can then be used to record pure rotational transitions in vibrationally and electronically excited states, with the resolution limited only by the radiative decay rate. Here, the sensitivity of this nearly-background-free technique is demonstrated by optically pumping the weak, nominally spin-forbidden CS $e\,{}^3\Sigma^- - X\,{}^1\Sigma^+$ (2-0) and $d\,{}^3\Delta - X\,{}^1\Sigma^+$ (6-0) electronic transitions while probing the CS $X\,{}^1\Sigma^+$ ($v''=0, J''=2\text{-}1$) rotational transition with millimeter waves. The $J'=2, N'=2 \leftarrow J'=1, N'=1$ pure rotational transition of the CS $e\,{}^3\Sigma^-$ ($v'=2$) state is then recorded by optically preparing the $J'=1, N'=1$ level of the $e\,{}^3\Sigma^-$ ($v'=2$) state via the $J'=1, N'=1 \leftarrow J''=1$ transition of the $e\,{}^3\Sigma^- - X\,{}^1\Sigma^+$ (2-0) band. © *2005 American Institute of Physics.* [DOI: 10.1063/1.2069865]

Because the frequencies of pure rotational transitions are easily calculated with high precision, the <1 MHz resolution of microwave sources makes rotational transitions straightforward to resolve and assign even in complex chemical environments, such as in discharges, where spectral congestion can hinder assignments of optical transitions. As a consequence, microwave transitions have been measured and tabulated[1,2] for a vast number of transient species, many of which have unknown optical transitions. Microwave-detected, microwave-optical double-resonance (MODR) techniques,[3–7] which monitor resonant changes in the microwave signal induced by optical pumping out of the lower or upper state of the rotational transition, are a convenient method of identifying optical transitions in these molecules. By labeling the molecule and the lower rotational level of the optical transition, microwave-detected MODR schemes provide a "rotational handle" to tremendously simplify the spectrum, allowing easier assignments and species identification. Moreover, microwave-detected MODR techniques are widely applicable; they can be applied to weak vibrational and electronic transitions and to transitions that have poor fluorescence quantum yields, which arise from nonradiative processes, such as collisional quenching, predissociation, intersystem crossing, or internal conversion. Once optical transitions are identified, microwave-detected MODR can then be used to measure the pure rotational spectra of optically populated vibrationally and electronically excited molecules, with the resolution limited only by the radiative decay rate.

Then, by monitoring the excited rotational transition, additional optical transitions from this state can be identified. Thus, microwave-detected MODR not only provides a rotational handle for identifying optical transitions, but it can also be used to map out the energy-level structure of the molecule by systematically bootstrapping through different vibrational and electronic transitions, with each vibronic level unambiguously labeled by its characteristic pure rotational transition.

Here, we report a new microwave-detected MODR technique applicable to the millimeter-wave frequency region called millimeter-detected, millimeter-wave optical polarization spectroscopy (mmOPS). mmOPS is analogous to optical polarization spectroscopy,[8] polarization labeling,[9] and microwave-optical polarization spectroscopy (MOPS),[10–12] in which the polarization of a probe beam is rotated by the angular anisotropy (unequal population in M_J sublevels) created by a polarized pump beam. Unlike previously reported polarization-detected techniques, however, in the current implementation of mmOPS, the polarization rotation is in the millimeter-wave beam, rather than the polarization rotation of an optical beam. We apply mmOPS to the well-known $A\,{}^1\Pi - X\,{}^1\Sigma^+$ electronic band system[13] of CS, which is produced in a pulsed discharge supersonic nozzle. We find that the near-zero background of mmOPS makes it more sensitive than the millimeter-wave-detected, millimeter-wave optical double-resonance (mmODR) technique,[5] especially when using a liquid-helium-cooled InSb detector.

Figure 1 is a schematic of the mmOPS apparatus. The experiment is performed in a $12 \times 12 \times 12$ in.^{3} vacuum chamber, which is evacuated by a 6 in. diffusion pump (Diff-

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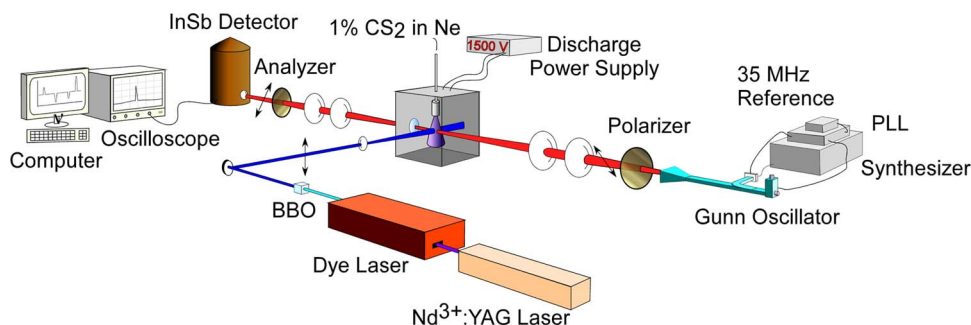
FIG. 1. Schematic of mmOPS experimental apparatus. The millimeter-wave source is a Gunn oscillator (73–106 GHz), stabilized and scanned by a phase-locked loop (PLL). The millimeter-wave radiation is collimated and focused by a pair of PFTE lenses (f=40 cm and f=30 cm, respectively) into a supersonic molecular beam produced from a pulsed dc discharge nozzle. After exiting the chamber, the millimeter-waves are recollimated and focused with another set of PFTE lenses (f=30 cm and f=40 cm, respectively) onto a liquid-helium-cooled InSb detector. The polarization rotation of the millimeter-waves is detected with nominally crossed freestanding wire grid polarizers.

stak 160, Edwards) backed by a rotary mechanical pump. CS is generated in a supersonic expansion by passing a mixture of 1% CS_2 in Ar through a pulsed discharge nozzle (1-mm-diameter orifice) that is similar to the design of Sanz *et al.*[14] The optimal experimental conditions for detection of the CS $X\,^1\Sigma^+(v=0, J=2-1)$ rotational transition are backing pressure (3 atm), nozzle pulse duration (350 μs), negative discharge voltage (1.4 kV), and discharge pulse (1 ms duration).

The millimeter-wave radiation is produced by a W-band (75–100 GHz) Gunn oscillator (J. E. Carlstrom Co.) that is phase-locked (XL Microwave 800A) to a harmonic of a microwave synthesizer (HP 8672A) and coupled through waveguide components to a calibrated attenuator (Hitachi W9513). The radiation is emitted into free space through a standard gain horn (TRG Control Data, 15 dB) with a linear polarization of 45° relative to the pump-laser polarization and focused by a pair of polytetrafluoroethylene (PTFE) lenses (f=40 cm, f=30 cm) to a spot size of ~1 cm diameter at the point of intersection with the molecular beam ~2 cm downstream from the nozzle. After exiting the chamber, the millimeter-wave beam is refocused by a second pair of PTFE lenses (f=30 cm, f=40 cm) onto a liquid-helium-cooled InSb hot-electron bolometer (Cochise Instruments). The bolometer output is digitized with a 500 MHz oscilloscope (LeCroy LC334A) and transferred to a computer for storage. The rotation of the millimeter-wave polarization is detected by a pair of nearly crossed freestanding wire grid polarizers. The polarizing grids are composed of 25-μm-diameter gold-plated tungsten wire with center-to-center wire spacings of 100 μm.[15] When perfectly crossed, the polarizers have an extinction ratio of ~10^{-3}.

The ultraviolet radiation is produced by frequency doubling the output of a Nd^{3+}:YAG-pumped dye laser (Quanta Ray DCR-3/Lambda Physik 3002) in a beta-barium borate (BBO) crystal. The doubled radiation (~1–1.5 mJ/pulse) is scanned ~10 cm^{-1} by pressure tuning (N_2) the etalon-narrowed oscillator cavity and is calibrated to ±0.01 cm^{-1} using a small amount of the residual fundamental to record an I_2 fluorescence spectrum.[16] As shown in Fig. 1, the vertically polarized ultraviolet radiation enters the vacuum chamber in a direction orthogonal to both millimeter-wave and molecular beams. The overlap of the optical field with the

millimeter-wave radiation is optimized by expanding the optical beam to ~2 cm in diameter in the overlap region.

Figure 2 shows selected rotational transitions from the CS $A\,^1\Pi-X\,^1\Sigma^+$ (1-0) vibrational band, obtained using the millimeter-detected mmODR [Fig. 2(a)] and mmOPS [Fig. 2(b)] techniques. In the mmODR technique, the millimeter-wave frequency is locked onto the CS $X\,^1\Sigma^+$ ($v''=0, J''=2-1$) rotational transition, and the absorption of the millimeter-wave radiation is monitored while the laser frequency is scanned. When the lower state of the optical transition is one of the two levels connected by the millimeter-wave transition, the sudden change in the ground-state population induced by the laser pulse creates a millimeter-wave transient nutation signal.[3–5] If the optical transition is out of the upper millimeter-wave connected level, then the transient nutation signal is absorptive (positive), whereas if the optical transition is out of the lower state, the transient nutation signal is emissive (negative). In addition to the five expected optical transitions originating from J''
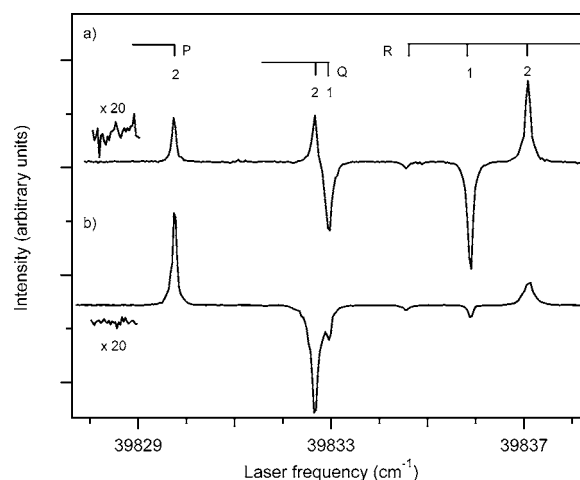

FIG. 2. Comparison of (a) the millimeter-wave-detected mmODR technique with (b) the millimeter-wave-detected mmOPS technique. The spectra are obtained by scanning the laser over the $A\,^1\Pi-X\,^1\Sigma^+$ (1-0) CS band, while the millimeter-wave frequency is locked to the CS $X\,^1\Sigma^+$ ($v''=0, J''=2-1$) rotational transition. The laser was scanned at the same rate for both spectra and each point is an average of 20 laser shots. The expanded baselines in the region of 39 829 cm^{-1} indicate that the baseline noise is improved by a factor of 4 for mmOPS relative to mmODR.

$=1[Q(1),R(1)]$ and $J''=2[P(2),Q(2),R(2)]$, Fig. 2(a) shows a negative-going transition at the expected position of the $R(0)$ line. The sign of the extra signal indicates that the optical transition out of $J''=0$ causes a preferential depopulation of the $J''=1$ level relative to the $J''=2$ level, which is most likely due to collisional ($J''=0$ hole filling from $J''=1$) population transfer following optical excitation. The optical pump can significantly alter the thermal population difference between the $J''=2$ and $J''=1$ levels because the CS $A\,^1\Pi-X\,^1\Sigma^+$ (1-0) transition is fully allowed and the Franck-Condon factor is 0.14.[13] As a consequence, both negative and positive mmODR signals are observed that are considerably larger than the original absorption signal in the absence of optical pumping.

The sensitivity of the mmODR experiments is limited primarily by the large and fluctuating CS absorption background caused by instabilities in the CS number density produced in the pulsed-discharge supersonic expansion. This CS production noise can be largely removed by using the mmOPS technique. When the vertically polarized pump laser is resonant with a CS electronic transition, it creates an anisotropic sample of CS molecules by preferentially pumping certain M_J states. If one of the levels of the millimeter-wave transition is in common with the pump-laser transition, then the vertical and horizontal components of the millimeter-wave probe are differentially absorbed, causing a polarization rotation of the millimeter waves. By using a set of crossed polarizers, the unrotated millimeter-wave radiation can be blocked, while only the rotated millimeter-wave radiation strikes the detector. Thus, the polarization-detected experiment can have a background level that is limited only by the imperfect extinction of the polarizers and the birefringence of the millimeter-wave transmission optics. When the polarizers are perfectly crossed, all mmOPS signals should have the same sign because millimeter-wave radiation strikes the detector only when the optical pump transition originates from one of the linked levels of the millimeter-wave transition. The signal levels in this case are often too small to be observed with the noise level of the current detector. As in optical polarization-based experiments,[17] however, the signal-to-background ratio can be improved by imperfectly crossing the polarizers to heterodyne the weak polarization-rotation signal field with the much stronger nonrotated field. Here, the spectra are collected at relatively large uncrossing angles ($\sim5°$) to obtain the best signal-to-background ratio. Although the background level at 5° is approximately twice the background level when the polarizers are perfectly crossed, the cross term between the signal and carrier millimeter-wave electric fields is much larger, which ultimately increases the signal-to-background ratio. The heterodyne term leads to both positive and negative features in the mmOPS spectrum. In contrast to the mmODR spectra, however, the sign and intensity of the observed features contain information about the rotational branch excited by the optical field. A detailed theoretical analysis (in the nonperturbative limit) of the expected intensities is currently in progress.[18]

The spectra in Fig. 2 have been normalized so that the strongest transition in each spectrum has the same peak intensity. The baseline in the region of 39 829 cm^{-1} is ex-
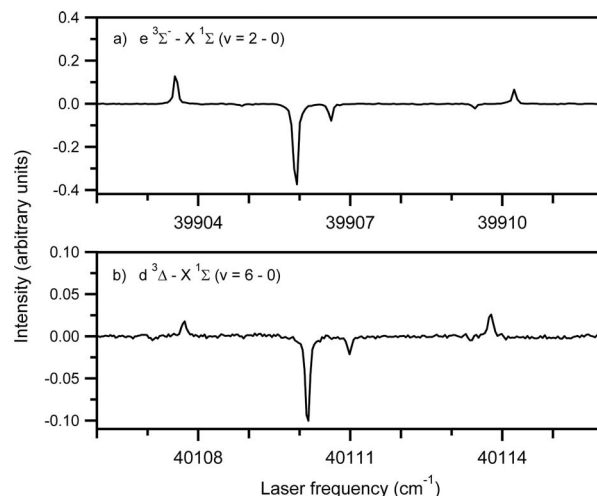

FIG. 3. mmOPS spectra of nominally spin-forbidden electronic transitions to triplet states of CS, which borrow their intensity via spin-orbit interactions with the $A\,^1\Pi$ state. The millimeter-wave frequency is locked to the CS $X\,^1\Sigma^+$ ($v''=0,J''=2-1$) rotational transition and the laser is scanned over the (a) $e\,^3\Sigma^--X\,^1\Sigma^+$ (2-0) and the (b) $d\,^3\Delta-X\,^1\Sigma^+$ (6-0) bands. The $e\,^3\Sigma^-$ ($v'=2$) and the $d\,^3\Delta$ ($v'=6$) states have 17% and 1% nominal $A\,^1\Pi$ character, respectively, for the rotational levels accessed (Ref. 13). Each point is an average of 20 laser shots.

panded to show that baseline noise is suppressed by a factor of 4 for mmOPS relative to mmODR. The enhancement in sensitivity (signal-to-background ratio) afforded by the mmOPS technique has enabled us to record nominally spin-forbidden optical transitions into triplet states of CS, as shown in Fig. 3. Although the sensitivity enhancement of mmOPS is largely due to the reduction of the CS production noise present in the CS ground-state mmODR signal, it is also improved because the millimeter-wave power incident to the molecular beam can be increased without saturating the millimeter-wave detector. In the absorption-detected technique the power of the Gunn oscillator is attenuated by approximately 15 dB to 600 μW to avoid saturation of the detector/preamplifier, while in the polarization-detected technique the full power of the oscillator (nominally 18 mW at 98 GHz) is incident to the molecular beam, but is attenuated by the crossed polarizers to <1 mW on the detector.

To demonstrate the additional capabilities of the mmOPS technique, we have measured a pure rotational transition in one of the optically populated triplet states. Figure 4 shows the mmOPS spectrum recorded with the laser populating the $J'=1$, $N'=1$ level of the $e\,^3\Sigma^-$ ($v'=2$) state. The trace is the average of four scans, each recorded by stepping the Gunn oscillator output in 50 kHz steps and averaging the bolometer output for ten laser shots at each frequency. The center frequency of the triplet rotational transition $J'=2$, $N'=2$ $\leftarrow J'=1$, $N'=1$ is determined to be 76 229.027(20) MHz. The measured linewidth is 1.3 MHz, which is significantly broader than the ground-state linewidth [~240 kHz full width at half maximum (FWHM)]. We attribute the additional linewidth to the radiative lifetime of the triplet state, which we expect to be ~1.2 μs, assuming that the lifetime is dominated by the $\sim17\%$ singlet character[13] of the populated "triplet" level and the 198 ns lifetime for the $A\,^1\Pi$ ($v=1$) state.[19]
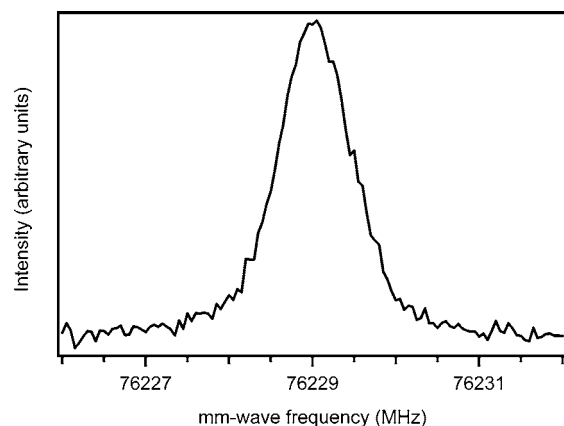
FIG. 4. Pure rotational mmOPS spectrum of an excited triplet state. The laser frequency is fixed to populate the $J'=1$, $N'=1$ level of the $e\,^3\Sigma^-$ state via the $J'=1$, $N'=1 \leftarrow J''=1$ transition of the $e\,^3\Sigma^- - X\,^1\Sigma^+$ (2-0) vibrational band. The center frequency of the pure rotational transition $J'=2$, $N'=2 \leftarrow J'=1$, $N'=1$ in the electronically excited state is 76 229.027(20) MHz.

In contrast to millimeter-wave transitions in the CS ground state, measurements of mmODR signals in the excited electronic state are not compromised by fluctuations in the background absorption of ground-state CS molecules. Rather, the main contributor to the baseline noise is the millimeter-detector noise, which is larger than the amplitude noise of the millimeter-wave source. Because the most significant advantage of the polarization-detected technique with the current millimeter-wave detector is the suppression of the CS source noise, the excited-state mmODR and mmOPS upper state spectra are nearly identical in quality. In addition to detector noise, both the mmODR and mmOPS techniques are artificially limited by the bandwidth (5 Hz–500 kHz) of the millimeter-wave detector. This limitation attenuates transient nutation signals with periods shorter than 2 μs and is particularly disadvantageous for the mmOPS technique, which would otherwise use the full power of the millimeter-wave source to induce the fastest possible transient nutation signals.

We have demonstrated that millimeter-wave-detected mmOPS is capable of being used to record selected rotational lines of an electronic transition with high sensitivity and to detect pure rotational transitions in electronically excited states, with resolution limited only by the radiative decay rate. In addition, the development of sensitive new techniques such as millimeter-wave-detected mmOPS makes it possible to observe and identify optical transitions in complex environments, such as discharges, where traditional one-color measurements can be limited by spectral congestion. We plan to extend the millimeter-wave-detected mmOPS technique to measure electric and magnetic moments of electronic and highly vibrationally excited states with Stark and Zeeman spectroscopy.

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